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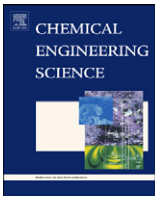

CO_2 capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol

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ABSTRACT

In this work, experimental data and a simplified vapor–liquid equilibrium (VLE) model for the absorption of CO_2 into aqueous solutions of piperazine (PZ) activated 2-amino-2-methyl-1-propanol (AMP) are reported. The purpose of the work was to find the AMP/PZ system with the highest concentration and cyclic capacity, which could be used in the industry without forming solid precipitations at operational temperatures. The effect of the AMP/PZ ratio and the total concentration level of amine was studied. The highest possible ratio of AMP/PZ, which does not form solid precipitates during the absorption of CO_2 at 40 °C (40 wt% amine), was identified. Considering the maximum loading found in the screening tests for AMP/PZ (3+1.5 M) and for 30 wt% MEA systems, the AMP/PZ system has about 128% higher specific cyclic capacity if operating between 40 and 80 °C, and almost twice the CO_2 partial pressure at 120 °C compared to MEA.

1. Introduction

Global warming is one of the most serious problems faced by earth at present. Anthropogenic CO_2 is one of the gases causing this problem, and its main sources stem from fossil fuel based power production (Desideri and Paolucci, 1999), traffic, iron and steel, cement production and the metal production based on reduction with carbon. CO_2 absorption in aqueous amine solutions is the most widely used process in the industry, and the most viable one at present. However, capital and operating costs are high, and in particular the heat required for absorbent regeneration. A better solvent may have higher CO_2 loading capacity, lower heat of absorption, faster absorption kinetics and favorable environmental properties. A combination of a secondary diamine (PZ) and a sterically hindered amine (AMP) can be expected to have high cyclic loading capacity combined with fast kinetics and possibly low heat consumption. Already, some investigations of AMP systems have been performed such as density and excess molar volumes (Chan et al., 2002), surface tension (Vazquez et al., 1997), enthalpy (Arcis et al., 2007) and pilot study (Gabrielsen et al., 2007). Piperazine has a higher reaction rate than the primary alkanolamines, due to its cyclic and diamine structure, and is often considered as promoter (Bishnoi and Rochelle 2000; Xu et al., 1998), but also as single amine (Plaza and Rochelle, 2010). Kinetics of CO_2 in PZ solutions were described by Derks et al. (2006). Sun et al. (2005) used a second-order reaction model for CO_2 and PZ, and a zwitterion mechanism for CO_2 and AMP. They also found that small additions of PZ significantly increased the absorption rate. Samanta and Bandyopadhyay (2009) have suggested a reaction mechanism for this system. It has also been shown that solutions of 2 amines may increase the absorption rates and reduce the solvent regeneration energy requirement (Chakravarty et al., 1985; Seo and Hong, 1996). The VLE data for the AMP/PZ 3/1.5 system was published also by Yang et al. (2010), but the temperature and the loading range were increased in this publication, and the data is fitted only with one function in the overall temperature and loading range.

2. Experimental section

Piperazine (≥ 98%) and AMP (≥ 97%), supplied by Fluka, were used for the experiments without further purification and dissolved in deionized water. The N_2 (99.6%) and CO_2 (99.999%) were supplied by AGA Gas GmbH.

The analysis of CO_2 in the liquid samples was done with the standard $BaCl_2$ method, see Ma'mun et al. (2006). A minimum of two parallel analyses were run, and if the difference was 3% or more, further analyses were run. The loading accuracy is estimated to be ±3.

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2.1. Screening tests

For comparison of the absorption rate and the loading capacity with other solvents, a screening apparatus was used (Aronu et al., 2009). The results were compared to the 30 wt% (5 M) monoethanolamine (MEA) solution. The absorption screening tests were performed at 40 ± 0.1 °C. The screening tests were perfomed in an apparatus as shown in Fig. 1. A mixture of N_2 and CO_2 passes through the amine, a part of the CO_2 is absorbed and the outlet gas phase CO_2 content is continuously recorded. From this an estimate of the absorption rate as function of time can be obtained as well as the capacity of the solvent The flows of N_2 and CO_2 were controlled by flow controllers (Bronkhorst High Tech—0.1% full scale), and these regulate also their mixing ratio. The CO_2 flow was set to 0.5 Nl/min and the N_2 flow to 4.5 Nl/min. This gave a 10% CO_2 concentration in the inlet gas flow through the amine solution. The volume of absorbent solution was set to 750 ml. The CO_2 content in the gas passing through the amine solution was measured by an IR detector (Rosemount Binos 100) and continuously logged by LabView software. An analyzer calibration run was performed before every measurement, and the two points used being pure N_2 and 10% CO_2. The program then registered the measured remaining CO_2 in the gas stream, and the difference between 0.5 Nl/min and the registered value by the IR instrument was saved as a function of time. The measurements were stopped when the measured outlet gas CO_2 concentration reached 95% of the initial value. After the end of absorption, a liquid sample was taken for measuring the CO_2 concentration and after desorption a sample was taken again and the density was measured. The analysis of the liquid phase CO_2 content served to control the mass balance. The desorption was performed at 80 °C, and the stripping gas was 100% N_2.

2.2. Vapor–liquid equilibrium tests (VLE)

For the equilibrium measurements two types of equipment were used. One atmospheric unit operating at 40, 60 and 80 °C, and a high pressure unit, operating up to 7 bar, for 100 and 120 °C.

The athmospheric glass apparatus consisted of 3 reactors each filled with 100–150 ml of preloaded amine solution (No. 2, 3 and 4 in Fig. 2). A gas phase consisting mainly of N_2 and CO_2 was circulated through the bottles until both temperature and CO_2 partial pressure were stabilized. For the measurements of the CO_2 concentrations in

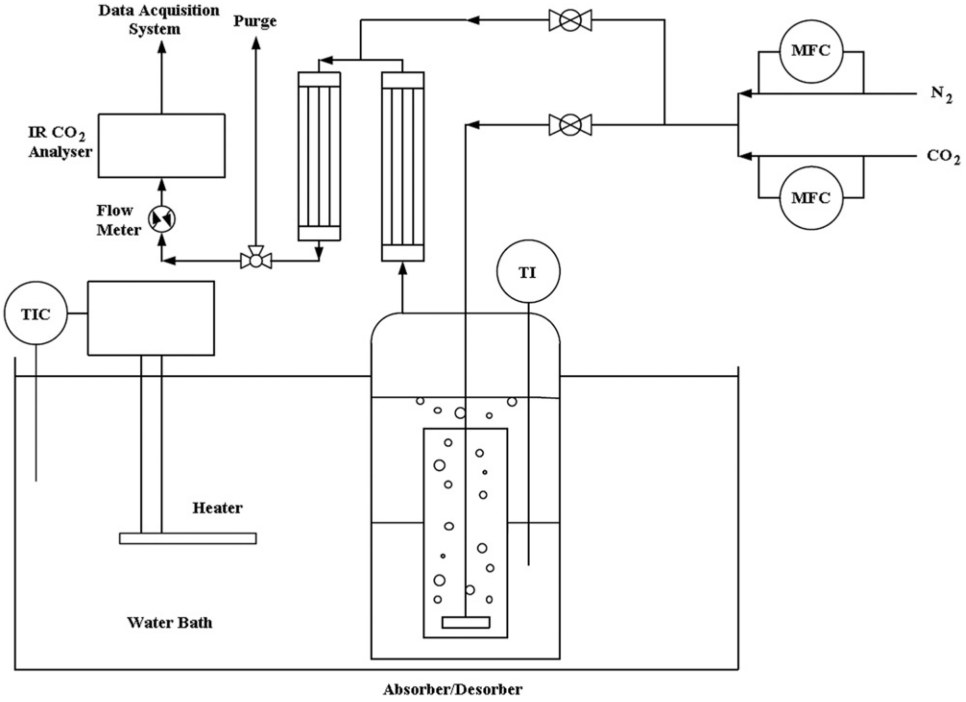

Fig. 1. Schematic of the screening apparatus Ma'mun et al. (2007).

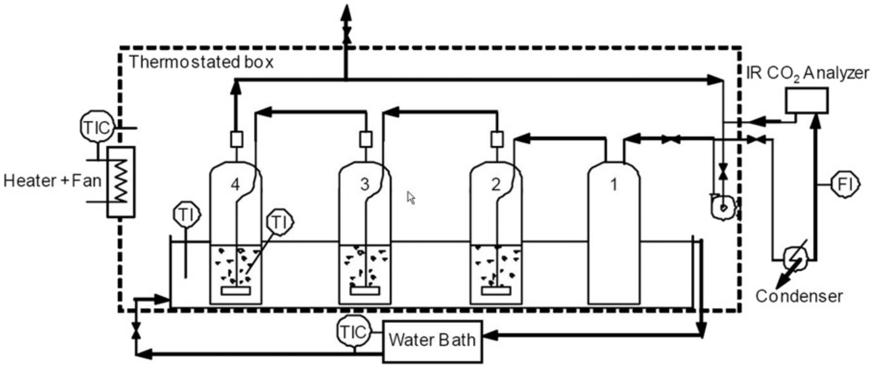

Fig. 2. Sketch of the atmospheric vapor–liquid equilibrium apparatus Ma'mun et al. (2006).